



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.ON THE OCCLUSION OF BARIC CHLORIDE BY
BARIC SULPHATE.

BY THEODORE WILLIAM RICHARDS AND HARRY GEORGE PARKER.

Presented January 9, 1894.

It has been known for a long time that baric sulphate possesses the power of carrying down other substances with it during the process of precipitation. Many experimenters have investigated with more or less accuracy the conditions which determine the amount of the occlusion in different cases, and have sought to eliminate as much as possible the error which the occlusion must introduce into analytical results.* Long ago, Fresenius found that some of the imprisoned salts, which could not be set free by any amount of washing of the freshly prepared baric sulphate, might be partially dissolved by water or acid after the precipitate had been ignited. Recently J. J. Phinney † has shown that in some cases, perhaps in all, this purifying process is only partial; hence it becomes important to discover a new method which may yield more satisfactory results. As Fresenius pointed out long ago,‡ the dissolving of the sulphate in sulphuric acid does not answer when barium salts are occluded.

The occlusion of baric chloride, the salt which is most generally used as the precipitant of sulphuric acid, has long been recognized. In most text-books upon quantitative analysis one is directed to pour the baric chloride into the sulphuric acid, and not *vice versa*; and it is generally understood that this precaution is in order to prevent as

* A partial bibliography of the subject is given by M. Ripper, *Zeitschr. für Anorg. Chem.*, II. 36. See also Jannasch and Richards, *Journ. f. prakt. Chemie*, [Neue Folge,] XXXIX. 321, XL. 236; E. A. Schneider, *Zeitschr. für Physikal. Chem.*, 1892, X. 425; Lunge, *Journ. f. prakt. Chemie*, XL. 239; F. W. Mar, *Am. J. Sci.*, [3.], XLI. 288; P. E. Browning, *Am. J. Sci.*, [3.], XLV. 399; J. J. Phinney, *Am. J. Sci.*, [3.], XLV. 468; Richards, *These Proceedings*, XXVI. 258; XXIX. 67, etc.

† *Am. J. Sci.*, [3.], XLV. 468.‡ *Zeitschr. Anal. Chem.*, IX. 52.

much as possible the error in question. It is also generally known that when the precipitate cakes together upon ignition, the occlusion has been large, and the result will usually be too high. But no systematic series of determinations of the conditions of experiment, and no exact method for wholly eliminating the error, have been devised and executed; hence the present work was undertaken with the idea of solving these difficulties.

In the course of an extended series of experiments upon the atomic weight of copper* finished several years ago, the attempt was made to determine the sulphuric acid in cupric sulphate by means of the usual analytical method. In order to correct the result for the occlusion of baric chloride, the precipitate, after having been weighed, was fused in pure sodic carbonate; and the chlorine in the aqueous solution of the residual cake was determined, calculated as baric chloride, and subtracted from the total weight of the precipitate.

The result in question was still vitiated by two opposite errors, the solubility of baric sulphate, and an incorrect atomic weight of barium, and hence it was rejected at the time. Nevertheless, the method seemed to be of value, and the stated intention of investigating it more closely has at last been carried out.

The objects of the present work were as follows:—

First, to discover if an accurate determination of sulphuric acid may be made by subtracting from the weight of the baric sulphate that of the baric chloride found in it; and

Second, to define the conditions which determine the amount of the occlusion, and thus to show how the error may best be avoided altogether.

A standard solution of pure sulphuric acid (containing 3.2 per cent of H_2SO_4) was used as the test substance, being weighed in tightly stoppered light glass bottles. The baric chloride used for its precipitation had been purified by repeated crystallization, and made up into another standard solution, which was used in appropriate quantities. The sodic carbonate was also recrystallized many times; and this substance, as well as the nitric acid and all other substances used in the chlorine determination, were proved to be free from the halogen.

The platinized brass weights used were standardized with great care, and the weighings were corrected to the vacuum standard. Due allowance was made in each case for the weight of the filter ash, and every precaution usual in ordinary analytical work was taken to in-

* These Proceedings, XXVI. 258.

sure accuracy. It is convenient to state first the experiments which determined the true strength of the standard acid, although these were made at a later stage of the work, when more experience had been gained.

In order to secure a standard of comparison which should be wholly different from the method under investigation, the strength of the sulphuric acid was determined alkalimetrically. Weighed portions of the solutions were almost neutralized with weighed portions of very pure gently ignited sodic carbonate, which had been crystallized ten times successively in platinum vessels. This neutralization was conducted in dilute solutions, so that there might be no loss of substance from the active effervescence. The dilute solutions were then evaporated to small bulk in platinum dishes, and the small excess of sodic carbonate required to complete the neutralization was added in dilute standard solution, methyl-orange being used as the indicator. This method, which may easily be made to give results accurate to within the hundredth of one per cent (one part in ten thousand) was devised for use in the investigation upon copper.

(1.) 18.6132 grams of the sulphuric acid solution required 0.6254 gram of dry sodic carbonate and 12.30 cubic centimeters of sodic carbonate solution (1 c. c. = 0.001793 gram of the salt), or in all 0.6475 gram for its neutralization.

(2.) 20.3966 grams of the acid solution required 0.6761 gram of dry sodic carbonate and 18.50 cubic centimeters of solution — in all 0.7092 gram of salt — for its neutralization.

The results of these analyses are precisely identical, each showing the acid solution to contain 3.214 per cent of H_2SO_4 . It was important now to determine whether under the most favorable circumstances similar results might be obtained from the usual method of precipitation. All the precautions necessary to make the occlusion of baric chloride as small as possible, which are discussed later, were practised, and a very slight excess only of baric chloride was used. The precipitates after long standing were washed with as little freshly distilled water as was necessary to free them from every trace of acid, and the filtrates (each measuring about a hundred and thirty cubic centimeters) were evaporated to very small bulk in platinum dishes, allowed to stand, and filtered through tiny filters in order to collect the baric sulphate which had been dissolved by the acid solution. Finally, the baric sulphate was all fused with pure sodic carbonate; and the aqueous extract was acidified with nitric acid. The chlorine was now precipitated as argentic chloride, which was collected and weighed upon a Gooch crucible.

(3.) 10.2107 grams of the solution gave 0.7804 gram of impure baric sulphate, collected upon a washed filter and ignited after the method of Bunsen. In the filtrate was found 0.0011 gram of additional precipitate. Only 0.0007 gram of argentic chloride was obtained from the whole of this substance.

(4.) 10.2189 grams of the solution yielded 0.7821 gram of precipitate, collected and ignited in a Gooch crucible.* The filtrates yielded 0.0017 more, and the whole of the baric sulphate gave 0.0024 gram of argentic chloride.

If these two determinations are not corrected for the occluded baric chloride, they give results for the strength of the acid solution which respectively equal 3.215 and 3.221 per cent of H_2SO_4 . When corrected for this error, they are reduced to 3.213 and 3.215; and the average of these corrected results, 3.214 per cent, is exactly equal to that found by alkalimetry.

It is evident that these experiments show clearly enough three facts: —

First, that, when the occlusion is small, the proposed method is capable of yielding results which are both consistent and accurate.

Second, that the solubility of baric sulphate may easily introduce an error of as much as one fifth of a per cent, even when this solubility is reduced to a minimum.

Third, that the strength of the standard solution being analyzed was very nearly 3.214 per cent.

These experiments do *not* show that the method is capable of giving a true result when the occlusion is large, nor do they show the circumstances which determine the amount of the intruding impurity. The first of these additional questions, which is suggested by the fact that pure baric chloride parts with some of its chlorine when heated in the air, will be treated next.

Throughout the following series of seventeen experiments the precipitation of the baric sulphate was conducted as usual very nearly at the boiling point of the solutions. The precipitates were digested for about an hour before filtering, and were each washed with nearly a litre of boiling water. The baric sulphate was always ignited with its filter paper; if the whole mass of the paper is charred by gentle heat before any active combustion is allowed, no trouble from reduction is

* When good asbestos is used, — and this is not always easy to obtain, — the Gooch crucible answers admirably for this purpose. Compare Jannasch and Richards, Mar, Browning, and Phinney, *loc. cit.* Ripper must have used a poor quality of asbestos (*Zeitschr. Anorg. Chem.*, II. 36).

encountered. In order to prove this, two portions of baric sulphate ignited with their respective filters were treated with a little sulphuric acid and ignited again. In neither case was a gain in weight observed. A comparison of experiment No. 3 with No. 4 shows the same fact; for in one of these experiments the precipitate was collected in the usual way, while in the other it was ignited in a capped Gooch crucible, where there was no chance of reduction.*

After the precipitate had been weighed, the chlorine present was determined in the manner used in Nos. 3 and 4. The results are given on the next page.

The reasons for the varied amounts of occlusion noticed in this table will be discussed later. At present it concerns us only to note that, while the variation in the uncorrected column is from 0.3198 gram (experiment No. 5) to 0.3247 gram (experiment No. 11), or 1.77 per cent, the corrected column shows an extreme difference of only 0.53 per cent (0.3192 in Nos. 5 and 12, to 0.3209 in No. 15). The seventeen experiments may be grouped into two series; one, where the occlusion is large, giving a corrected average of 0.3199 (Nos. 7, 8, 9, 10, 11, 12, 13); the other, where the occlusion is small, giving a corrected average of 0.3201 (Nos. 5, 6, 14, 15, 16, 17, 18, 19, 20, and 21). The close agreement of these averages is sufficient proof that the method is capable of giving satisfactory results even when the occlusion is very large, and hence that no essential amount of the occluded chlorine in baric sulphate is liberated upon ignition.

The individual variations are no doubt chiefly caused by the solubility of baric sulphate in the acid solution from which it came, as is the deficiency of nearly 0.5 per cent in the final average. It is to be noted that in Nos. 14, 15, 16, and 17, where the average is higher than the others, a large excess of baric chloride, which must diminish the solubility of the sulphate, was used. The amount dissolved was not determined in any case, as the results were intended to represent the usual method of analysis, and were rather to be compared with one another than with an absolute standard.

It is interesting to note, however, that when the precipitation is conducted with reasonable care — as in Nos. 14 to 21, — the

* This observation does not agree with that of M. Ripper (*Zeitschr. Anorg. Chem.*, II. 36). It is possible that Ripper conducted his combustion at too high a temperature; at any rate, it is true, as he observes, that a slight reduction would make much more difference in his work than in such as ours.

TABLE OF RESULTS.

SERIES I.

No. of Experiment.	Amount of Solution taken.	Mixed Precipitate.	AgCl.	H ₂ SO ₄ per 10 Grams of Solution.	
				Uncorrected.	Corrected.
5	12.1626	0.9262	.0025	.3198	.3193
6	11.6573	0.8913	.0032	.3211	.3203
7	13.4319	1.0306	.0091	.3223	.3202
8	11.8821	0.9096	.0071	.3215	.3197
9	10.1826	0.7866	.0143	.3244	.3202
10	10.1820	0.7844	.0137	.3236	.3194
11	10.1962	0.7881	.0152	.3247	.3201
12	10.2144	0.7870	.0149	.3236	.3192
13	10.2030	0.7887	.0133	.3246	.3207
14	10.1920	0.7800	.0039	.3214	.3202
15	10.2454	0.7853	.0032	.3219	.3209
16	10.2470	0.7840	.0039	.3214	.3202
17	10.2214	0.7828	.0046	.3216	.3203
18	10.1846	0.7789	.0039	.3212	.3200
19	10.1846	0.7788	.0042	.3212	.3199
20	10.2286	0.7850	.0057	.3223	.3206
21	10.2166	0.7812	.0052	.3212	.3196
True amount of H ₂ SO ₄ present . .				.3214	

amount of the error due to occlusion usually almost balances the error due to the solution of the precipitate, so that the final uncorrected result closely approximates the true one. The average of these uncorrected results is 0.3215 instead of 0.3214.

Since the amount of argentic chloride obtained from four fifths of a gram of baric sulphate varied from 0.0005 gram (No. 3) to 0.0152 gram (No. 10), it becomes important to define the exact circumstances

of the occlusion. Many of the experiments above were made with this idea in view.

The two experiments numbered 18 and 19 may be taken as types of the usual method of working. The volume of the sulphuric acid was about fifty, and that of the baric chloride about twenty cubic centimeters; the latter solution was slightly in excess, and was poured gradually into the former.

SERIES II.

No. of Experiment.	Mixed Precipitate.	Argentio Chloride.	AgCl per Gram of Precipitate.
18	gram. .7789	gram. .0039	gram. .0050
19	.7788	.0042	.0054
Average0052

In order to determine whether an excess of baric chloride increases the occlusion, a similar series was made, using twice the amount of baric chloride necessary for the precipitation.

SERIES III.

No. of Experiment.	Mixed Precipitate.	Argentio Chloride.	AgCl per Gram of Precipitate.
14	gram. .7800	gram. .0039	gram. .0050
15	.7853	.0032	.0041
16	.7840	.0039	.0050
17	.7828	.0046	.0059
Average0050

Since this average is not greater than the last (0.0052), no occlusion could have taken place after the precipitation was complete, and the only effect of the excess of baric chloride was to diminish the solubility of the precipitate (see page 71).

In the next series the sulphuric acid was poured into the baric chloride, instead of *vice versa*.

SERIES IV.

No. of Experiment.	Mixed Precipitate.	Argentio Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
9	.7866	.0143	.0182
10	.7844	.0137	.0175
11	.7881	.0152	.0193
22	.7832	.0156	.0199
Average0187
Average of Series II. and III. . .			.0051

These results prove the necessity of the old rule, which directs that the baric salt should always be added to the sulphate, if any proof of this was needed.

In all these experiments a small amount—perhaps the quarter of a cubic centimeter—of strong hydrochloric acid was added to the sulphuric acid before precipitation. In order to determine if this acid might have had some effect upon the occlusion, four experiments were made in which the amount of this acid was very much increased. In Nos. 12 and 13 about ten cubic centimeters of strong acid were used, and in Nos. 23 and 24 fully twenty. The first two were allowed to stand a

SERIES V.

No. of Experiment.	Mixed Precipitate.	Argentio Chloride.	AgCl per Gram of Precipitate.
	gram.	gram.	gram.
12	.7870	.0149	.0189
13	.7887	.0133	.0169
23	.7211	.0266	.0369
24	.7236	.0223	.0306
Average0264
Average of Series II. and III. . .			.0051

long time, in order that the precipitate, which separates slowly from strongly acid solutions, might have time to deposit; while the second two were filtered within an hour, with the loss of nearly ten per cent of the precipitate.

Thus the presence of free hydrochloric acid increases the occlusion to an enormous extent.

In order to determine the effect of dilution, other circumstances remaining the same, two precipitations were made from solutions like those of Series II., diluted fourfold with water.

SERIES VI.

No. of Experiment.	Mixed Precipitate.	Argentie Chloride.	AgCl per Gram of Precipitate.
25	gram. .7676	gram. .0023	gram. .0030
26	.7701	.0024	.0031
Average0031
Average of Series II. and III. . .			.0051

Hence, the more dilute the solutions, the less is the occlusion.

In all the preceding cases the precipitate was allowed to run down the side of the beaker in an excessively fine stream, with continual stirring. This procedure had been shown in preliminary experiments to be even more efficacious as a means of diminishing occlusion than the addition of the precipitant in definite drops, no matter how slowly. Two experiments, in which the baric chloride was poured in with great rapidity, close the data to be presented.

SERIES VII.

No. of Experiment.	Mixed Precipitate.	Argentie Chloride.	AgCl per Gram of Precipitate.
20	gram. .7850	gram. .0057	gram. .0073
21	.7812	.0052	.0067
Average0070

As was to have been expected, the impurity is greater here than in Series II., III., and VI., but less than in Series IV. and V.

It was not the intention of this paper to extend the investigation to the study of the occlusion of other chlorides, which must necessarily complicate the problem greatly. It is very interesting to note that the amount of occlusion seems to be due rather to the amount of chlorine present than to the amount of barium, for hydrochloric acid increased the occlusion almost as much as an equivalent amount of baric chloride did. This observation leads one to conclude that a careful study of the phenomenon from a physico-chemical point of view might furnish some satisfactory clue as to the nature of such occlusion in general; and it is hoped that before long a collection of suitable data upon the problem may be obtained here.* The present paper deals only with the solving of an analytical problem.

At first sight, the facts shown by this paper appear to be contradictory to those stated by F. W. Mar,† who recommends the use of strong nitric and hydrochloric acids for the precipitation. It must be borne in mind, however, that Mar was precipitating the barium with an excess of sulphuric acid, and hence that a considerable amount of occlusion could make very little difference in his case. When one is determining sulphuric acid by means of an excess of barium, nothing could be worse than the addition of a large amount of hydrochloric acid; and this point cannot be too strongly emphasized.

Mar rightly states that a considerable excess of sulphuric acid is necessary to secure rapid precipitation of all the barium in strongly acid solutions. If Fresenius had realized that an excess of a common ion in solution decreases the solubility of a precipitate, he would not have confounded the solubility of baric sulphate in a strong solution of baric chloride with its solubility in pure water,‡ or in water containing free hydrochloric acid.

The conclusions reached in the present paper are as follows:—

First, that the occlusion of baric chloride by baric sulphate may lead to very serious error.

Second, that the amount of this occlusion is greater in concentrated than in dilute solutions, greater in the presence of hydrochloric acid than in its absence, and greater when the sulphate is poured into the

* For the treatment of an analogous case, see E. A. Schneider, *Zeitschr. Phys. Chem.*, X, 425.

† *Am. J. Sci.*, [3.], XLI, 288, XLV, 399.

‡ *Zeitschr. f. Anal. Chem.*, IX, 52.

barium salt than when the pouring takes place in the opposite direction.

Third, that under the usual conditions of careful precipitation in the presence of a small amount of free acid, the error from occlusion is almost balanced by the solubility of baric sulphate in acids and water, which solubility must be considered in careful work.

Fourth, that the error due to this occlusion may be corrected with great exactness by determining the amount of chlorine held by the precipitate, and subtracting the corresponding amount of baric chloride from the total weight of the precipitate.

The occlusion of iron and other substances by baric sulphate is being further studied in this Laboratory.